THE SYNTHESIS OF p-PHENYLENEDIIMIDO COMPLEXES OF RHENIUM(V)

by

CHANGMIN KIM
B.S., Seoul National University, Korea, 1983

A THESIS

submitted in partial fulfillment of the
requirements for the degree

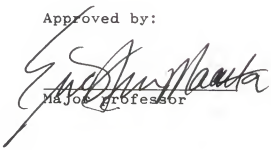
MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1988

Approved by:



Major Professor

CONTENTS

LIST OF FIGURES

LIST OF TABLES

I. INTRODUCTION

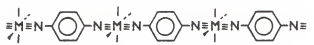
Polymeric compounds, which have a delocalized pi-system through the whole molecule, have been the subjects of intense research activity in recent years because of their possibility as one-dimensional conductors[1]. Among them, polyacetylene is the most extensively studied conducting polymer. Its electrically conducting nature was predicted when it was synthesized first from acetylene in 1955[2]. But the intense study on conducting polymers has been spurred since the series of reports of the achievement of a highly conducting "metallic" state upon doping of polyacetylene in 1977[3].

On the other hand, transition metal complexes of macrocyclic compounds, such as phthalocyanine or porphyrin, show good conductivity when metal centers are linked by bridging ligands, which have delocalized pi-electron[4]. The bridging ligands are difunctional sigma donors, such as pyrazine, bipyridine, or diisocyanobenzene.

While the use of pyrazine and related bridging groups has led to a variety of interesting and important developments, the macrocyclic system imposes certain limitations[5]. The use of metallomacrocyclic complexes limits the variation of ligand systems and the use of high-valent metal complexes. Furthermore, it is often observed that coordination of a metal complex to one end of the

difunctional sigma donor bridge results in a diminished binding constant for coordination of the remaining donor site and dissociation into mononuclear species is often observed in solution[6].

Our initial studies were focused on trans-diimido complexes bridged by arene:

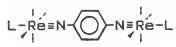


In this model system, the dissociation problem could be eliminated, since the imido ligand binds to the metal via formal M≡N- triple bonds. Furthermore a systematic study of conducting nature could be possible since not only a lot of high valent metals can be used but the substitution of spectator ligands is much easier; and we may be able to tailor the best conducting system.

Transition metal complexes containing organoimido ligands were first reported in 1959[7]. Since then, a number of synthetic routes have been used to make organoimido complexes, and several of them seem to have some degree of generality[8]. However, transition metal complexs which have two imido ligands on one metal at trans position have not been reported yet; only some cis-diimido complexes, $Mo(NR)_2(S_2CNEt_2)_2$[9] and $OsO_2(NR)_2$[10], and oxo bridged trans complex, $(PhN)(Et_2NCS_2)_2Re\text{-}O\text{-}Re(S_2CNEt_2)_2(NPh)$[11], were made. We tried several ways to make trans-diimido

complexes of rhenium, but none of them were successful[see Appendix].

Another route to make a polymeric system bearing the transition metal-imido skeleton is to use monomeric p-phenylenediimido complexes:



Polymerization can be achieved by replacing ligand L which is trans to imido ligand with bridging ligands, such as oxo or acetylenic ligands.

An aryl diimido bridged dimetal complex was first prepared in the form of $(S_2P(OEt)_2)_3Mo{\equiv}N\text{-}C_6H_4\text{-}N{\equiv}Mo(S_2P(OEt)_2)_3$ [12] and some more p-phenylenediimido complexes of Mo were made recently[13]. The nature of the bridging bonding in an Mo(III) derivative, $Cl(Me_3P)_4Mo{\equiv}N\text{-}C_6H_4\text{-}N{\equiv}Mo(PMe_3)_4Cl$, has been investigated by Extended Hückel techniques and the nature of the HOMO is shown below[5]:

The d_{yz} orbitals on each Mo, P_y orbitals of nitrogen, and pi-orbitals of arene ring take part in pi-system conjugation. It was predicted from this system that a polymeric system made by linking these dimeric compounds could show conducting nature[5].

One of the best ways to make organoimido complex is the conversion of oxo complex, which has the isoelectronic structure with imido complex:

$$M{=}O + RNH_2 \longrightarrow M(NR) + H_2O$$

$$M{=}O + RN(SiMe_3)_2 \longrightarrow M(NR) + (Me_3Si)_2O$$

$$M{=}O + R'_3P{=}NR \longrightarrow M(NR) + R'_3PO$$

$$M{=}O + RNCO \longrightarrow M(NR) + CO_2$$

$$M{=}O + RNSO \longrightarrow M(NR) + SO_2$$

This thesis reports the preparation of u-p-phenylene-diimidobis[trichlorobis(triphenylphosphine)rhenium(V)] from an oxo rhenium(V) complex and p-phenylenebis (phosphineimine). The conversion of this complex to several p-phenylene diimido complexes has been investigated. The polymerization reactions of these diimido complexes also have been studied.

II. THE PREPARATION AND CHEMISTRY OF p-PHENYLENEDIIMIDO COMPLEXES

Experimental Section

The majority of the newly made Re complexes were not sensitive to air nor moisture, but all reactions were routinely carried out in an atmosphere of dry nitrogen with use of dry, freshly distilled solvents. Infrared spectra were recorded in Nujol mulls with a Perkin-Elmer 1330 spectrophotometer and were calibrated with use of a polystyrene film. Proton NMR spectra were recorded on a Bruker WM-400 spectrometer in $CDCl_3$ solution. Chemical shifts are reported in parts per million downfield of internal tetramethylsilane(TMS) standard. Elemental analysis were carried out by Galbraith Laboratories, Inc.. The ^1H NMR data for the new Re complexes are listed in Table 1(pp. 31-33).

$ReOCl_3(PPh_3)_2$ was prepared according to the literature method[14]. The preparations of $Ph_3P{=}N{-}C_6H_4{-}N{=}PPh_3$ and tetra(cyclohexyl)thiuram disulfide are mentioned below. All other starting materials were purchased from Aldrich Chemical Company.

$Ph_3P{=}N{-}C_6H_4{-}N{=}PPh_3$

This compound was made by a modification of the literature method[15] as follows. To 1.0g(3mmole) of p-phenylenediazide dissolved in 50mL of diethyl ether was added slowly 6.4g(12mmole) of tripheny phosphine dissolved in 50mL of ether while stirring. The mixture was stirred for 2 hours at room temperature and the yellow precipitate was filtered and washed with ether. p-Phenylenediazide was prepared according to the same literature method except using HBF_4 instead of $NaBF_4$ and HCl.

^1H NMR; 6.52ppm(s: 4H), 7.38ppm(m: 12H), 7.46ppm(m: 6H), 7.70ppm(m: 12H). (s=singlet, m=multiplet)

IR; 1590(w), 1491(s), 1317(s), 1236(w), 1187(w), 1107(s), 1051(s), 1028(w), 1003(m), 825(m), 762(w), 754(w), 718(s), 699(s), 679(m), 654(w), 541(s), 529(s), 493(w). (s=strong, m=medium, w=weak)

Tetra(cyclohexyl)thiuram disulfide.

To 50 mL of ethanol containing dicyclohexylamine (36.27g, 0.2mmole) and CS_2(12mL, 0.2mmole) was added slowly 50% solution of NaOH(8g). The mixture was stirred for 6 hours at room temperature and white precipitate, $NaS_2CN(C_6H_{11})_2$, was formed. The precipitate was filtered and washed with hexane. 10g(36mmole) of $NaS_2CN(C_6H_{11})_2$ was added to 100 mL of ethanol containing 4.5g(16mmole) of I_2 while stirring. The color was changed immediately from deep

red to pale yellow. The mixture was stirred for additional 2 hours at room temperature. The pale yellow precipitate was filtered and washed with water.

IR; 1632(m), 1489(s), 1304(s), 1244(m), 1169(m), 1157(m), 1107(s), 1040(m), 1029(w), 995(m), 973(w), 959(w), 902(m), 877(s), 840(w), 804(w), 686(m), 578(w), 491(w).

$Cl_3(PPh_3)_2Re{\equiv}N\text{-}C_6H_4\text{-}N{\equiv}Re(PPh_3)_2Cl_3$ (1).

$ReOCl_3(PPh_3)_2$ (5.0g, 6.0mmole) and $Ph_3P{=}N\text{-}C_6H_4\text{-}N{=}PPh_3$ (1.9g, 3.0mmole) were refluxed for 4 hours in 300 mL of dry benzene. The precipitate was filtered and washed with benzene and several portions of acetone until the dark color of the filtrate solution became lighter. After drying under vacuum, 3.6g of brown product was obtained(yield:69%).

Anal: Calcd. for $C_{78}H_{64}Cl_6N_2P_4Re_2$; C:53.89, H:3.71, N:1.61. Found; C:53.83, H:3.73, N:1.80.

IR; 1589(m), 1575(m), 1483(m), 1437(s), 1197(m), 1165(m), 1122(w), 1095(s), 1089(w), 1035(m), 1021(m), 1006(m), 859(m), 750(s), 697(s), 627(w), 579(w), 526(s), 518(s), 502(s).

$Cl(Et_2NCS_2)_2Re{\equiv}N\text{-}C_6H_4\text{-}N{\equiv}Re(S_2CNEt_2)_2Cl$ (2a).

To 100 mL of benzene containing 4.3g(15mmole) of tetraethylthiuram disulfide was added 3.2g(1.8mmole) of compound 1. The reaction mixture was refluxed for 8 hours. The precipitate was filtered and washed with benzene and

acetone. After drying under vacuum, 1.6g of very dark brown product was obtained(yield:78%).

Anal: Cacld. for $C_{26}H_{44}Cl_2N_6Re_2S_8$; C:27.38, H:3.89, N:7.37. Found; C:27.71, H:3.80, N:6.91.

$Cl((i\text{-}Pr)_2NCS_2)_2Re{\equiv}N\text{-}C_6H_4\text{-}N{\equiv}Re(S_2CN(i\text{-}Pr)_2)_2Cl$ (2b).

To 100mL of benzene containing 4.1g(12mmole) of tetra(isopropyl)thiuram disulfide was added 2.0g(1.2mmole) of compound 1. The reaction mixture was refluxed for 8 hours. The precipitate was filtered and washed with benzene and acetone. After drying under vacuum, 1.3g of brown product was obtained(yield:86%).

IR; 1590(w), 1495(s), 1336(s), 1198(s), 1149(s), 1125(m), 1045(s), 1025(s), 848(s), 781(m), 699(m), 621(w), 589(s), 535(m), 487(w).

$Cl((C_6H_{11})_2NCS_2)_2Re{\equiv}N\text{-}C_6H_4\text{-}N{\equiv}Re(S_2CN(C_6H_{11})_2)_2Cl$ (2c).

To 100 mL of benzene containing 2.0g(3.9mmole) of tetra(cyclohexyl)thiuram disulfide was added 1.5g(0.87mmole) of compound 1. The reaction mixture was refluxed for 12 hours. The precipitate was filtered and washed with acetone. After drying under vacuum, 1.2g of red-brown product was obtained(yield:88%).

$Cl(Me_2NCS_2)_2Re{\equiv}N\text{-}C_6H_4\text{-}N{\equiv}Re(S_2CNMe_2)_2Cl$ (2d).

To 100mL of toluene containing 2.6g(11mmole) of tetramethylthiuram disulfide was added 2.0g(1.2mmole) of compound 1. The reaction mixture was refluxed for 24 hours. The dark brown precipitate was filtered and washed with acetone.

$(EtO)(Et_2NCS_2)_2Re{\equiv}N\text{-}C_6H_4\text{-}N{\equiv}Re(S_2CNEt_2)_2(OEt)$ (3a).

0.1g(4.3mmole) of freshly cut Na metal was dissolved in 100mL of dry ethanol. 0.5g(0.44mmole) of compound 2a was added and the reaction mixture was refluxed for 6 hours. The precipitate was filtered and washed with ethanol and pentane. After drying under vacuum, 0.31g of yellow product was obtained(yield:61%).

IR; 1507(m), 1274(s), 1214(m), 1155(m), 1108(m), 1067(m), 1014(m), 917(m), 851(m), 787(w), 550(m).

$(EtO)((i\text{-}Pr)_2NCS_2)_2Re\ N\text{-}C_6H_4\text{-}N\ Re(S_2CN(i\text{-}Pr)_2)_2Cl$ (3b).

0.14g(6.0mmole) of freshly cut Na metal was dissolved in 100mL of dry ethanol. 1.0g(0.79mmole) of compound 2b was added and the reaction mixture was refluxed for 3 hours. The precipitate was filtered and washed with ethanol and pentane. After drying under vacuum, 0.55g of bright yellow product was obtained(yield:55%).

$(EtO)((C_6H_{11})_2NCS_2)_2Re{\equiv}N-C_6H_4-N{\equiv}Re(S_2CN(C_6H_{11})_2)_2(OEt)$ (3c).

0.018g(0.76mmole) of freshly cut Na metal was dissolved in 50mL of dry ethanol. 0.2g(0.13mmole) of Compound 2c was added and the reaction mixture was refluxed for 6 hours. 0.15g of yellow product was obtained.

$(CH_3-C_6H_4-O)(Et_2NCS_2)_2Re\equiv N-C_6H_4-N\equiv Re(S_2CNEt_2)_2(O-C_6H_4-CH_3)$ (4a).

To 100mL of methylene cholride containing 0.23g (2.2mmole) of p-cresol was added 0.5g(0.43mmole) of compound 3a. The reaction mixture was stirred for 10 hours and filtered. The volume of the filtrate was reduced to 10mL and 100 mL of diethyl ether was added to precipitate the product. The precipitate was filtered and washed with ether thoroughly. After drying under vacuum, 0.32g of dark brown product was obtained(yield:53%).

$(CH_3-C_6H_4-O)((i-Pr)_2NCS_2)_2Re\equiv N-C_6H_4-N\equiv Re(S_2CN(i-Pr)_2)_2(O-C_6H_4-CH_3)$ (4b).

To 100mL of methylene chloride containing 0.21g (2.0mmole) of p-cresol was added 0.5g(0.39mmole) of compound 3b. The reaction mixture was stirred for 10 hours and filtered. The volume of the reddish brown filtrate was reduced to 10mL and 100mL of diethyl ether was added to precipitate the product. The precipitate was filtered and washed with ether thoroughly. After drying under vacuum,

0.30g of reddish brown product was obtained(yield:55%).

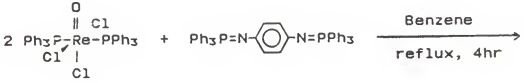
Anal: Calcd. for $C_{48}H_{74}N_6O_2Re_2S_8$; C:41.30, H:5.34, N:6.02.

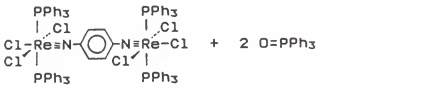
Found; C:41.34, H:5.33, N:5.93.

IR; 1601(w), 1505(m), 1489(s), 1335(s), 1273(s), 1198(m), 1166(w), 1152(s), 1125(w), 1098(w), 1045(m), 1023(m), 876(m), 853(m), 832(m), 800(w), 785(m), 588(m), 546(m).

Results and Discussion

$ReOCl_3(PPh_3)_2$ reacts with $Ph_3P{=}N{-}C_6H_4{-}N{=}PPh_3$ in refluxing benzene to give the p-phenylenediimido complexe, 1, which is air-stable:





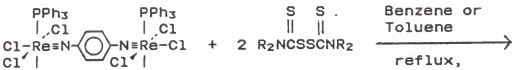
(1)

1

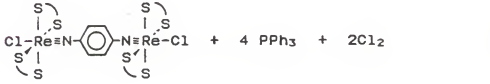
Several kinds of configurational isomers are possible for this complex. But in the related monomeric system, two

PPh_3 ligands on one rhenium are trans to each other and the imido ligand is trans to chloro ligand[16]. The ^1H NMR spectrum, which has a sharp singlet for the 4 phenylene protons at 6.52ppm(Figure 1), excludes the possibility of scrambling of ligands at each metal center.

Complex 1 reacts with tetraalkylthiuram disulfides to give complex 2:



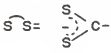
1



(2)

2

Where, R= CH_3, C_2H_5, $CH(CH_3)_2$, or cyclohexyl



Surprisingly, thiuramdisulfides with more bulky alkyl groups are more reactive. In the case of tetraisopropyl or tetra(cyclohexyl)thiuram disulfide, carbamate complexes were formed smoothly in refluxing acetone. But the reaction of tetramethylthiuram disulfide required higher reaction

temperature and longer reaction time. This may reflect the greater solubility of the complexes with larger alkyl groups.

Two isomeric structures are possible for complex 2:

trans cis

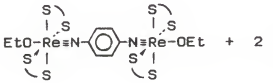
But a sharp ^1H NMR singlet peak for the 4 phenylene protons tells us that the ligand arrangement on both sides is the same. In the case of the diethyldithiocarbamate complex, the ^1H NMR spectrum shows a sharp singlet for 4 phenylene protons at 7.33ppm, two sets of multiplets at 3.86 and 3.71ppm, and a triplet at 1.38ppm(Figure 3). This is the typical spectrum of an ABX_3 type system for the diethyl dithiocarbamate ligands. This ^1H NMR spectrum and the ^{13}C NMR spectrum were not changed when the temperature was lowered to -30°C at which temperature cis-trans conversion should be restricted. From this evidence we can exclude the possibilities of either a cis-isomer or a fast interconversion of trans- and cis-isomers.

It is believed that pi-electron delocalization can occur through Re, N, arene, N, and Re axis. If we take N-Re-Cl axis as a z axis, six valence orbitals of each Re,

$5d_{z^2}$, $5d_{x^2-y^2}$, 6s, $6p_x$, $6p_y$, and $6p_z$, form -bonds with the six ligands. Then two d-electrons of each Re occupy the d_{xy} orbital leaving d_{xz} and d_{yz} orbitals for overlapping with p_x and p_y orbitals of the nitrogen. This explains the formal N Re triple bond and also the diamagnetism of this compound.

The chloro ligand of compound 2 is relatively labile and can be replaced easily. An ethoxy ligand can be substituted for a chloro ligand to produce compound 3:

2



(3)

3

Unlike the other diimidorhenium complexes made, species 3 is very sensitive to moisture. It reacts with water to cause the substitution of hydroxy group for ethoxy group:

(4)

3 3'

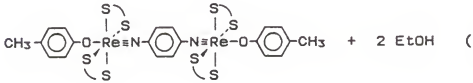
Species 3', which has not been observed but is believed to be a fairly good proton donor, attacks another ethoxy group and an exciting polymerization occurs:

$$L_nRe\text{-}OH + L_nRe\text{-}OEt \longrightarrow L_nRe\text{-}O\text{-}ReL_n + EtOH \qquad (5)$$

This reaction is mentioned in more detail in next section.

Complex 3 reacts with p-cresol, which has fairly acidic proton, to give complex 4:

3

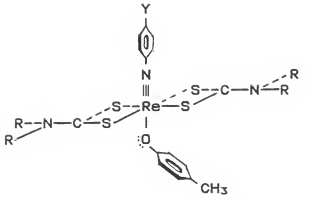


4

(6)

^{1}H NMR Spectra and elemental analysis result nicely agree with the product 4. In the case of di(iso-propyl)dithio carbamato complex, the ^{1}H NMR Spectrum shows two broad peaks for iso-propyl protons. It is believed that the restricted rotation about $S_2C\text{-}NR_2$ bond causes the broadening of the peaks. The schematic representation of this complex is

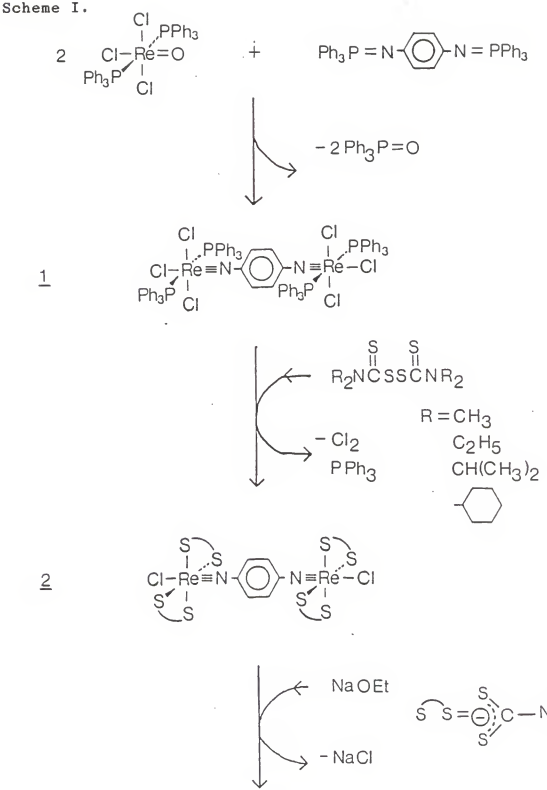
shown below:



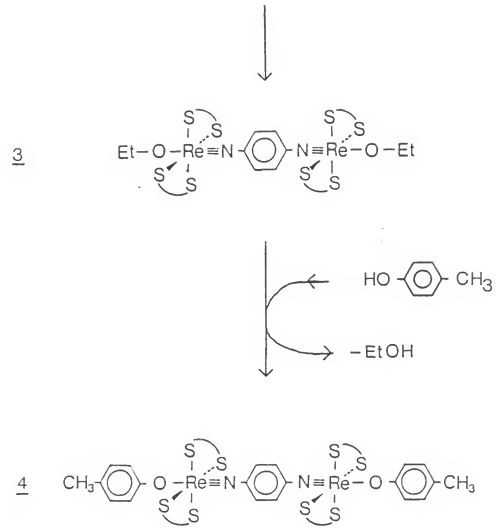
When the temperature was lowered to -30°C, the ^{1}NMR peak of the CH protons split into two separate peaks at 4.93ppm and 5.25ppm. The splitting of the dtc methyl proton peaks showed the overlap of 8 different peaks from 8 different methyl groups(Figure 10).

Scheme I shows the overall reaction pathway. The ^{1}H NMR spectra of diimido complexes are shown in Figure 1 to Figure 9.

Scheme I.


2
+
$Ph_3P=N$
$N=PPh_3$
$-2\,Ph_3P=O$
1
$R_2NCSSCNR_2$
R = CH_3
C_2H_5
$CH(CH_3)_2$
$-Cl_2$
PPh_3
2
NaOEt
$-NaCl$

Scheme I. (Continued)



Figures 1 - 9. ^{1}H NMR Spectra of p-Phenylenediimido Complexes of Rhenium.

Figure 1.

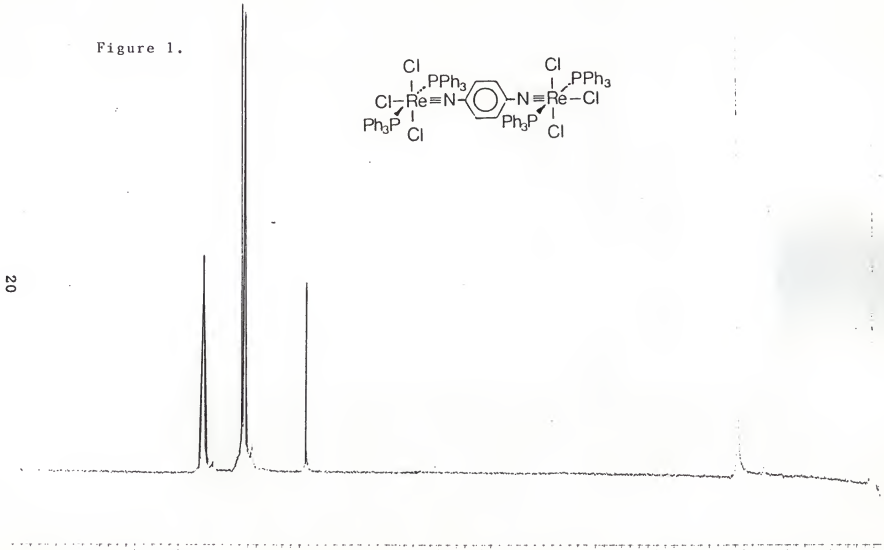
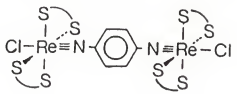


Figure 2.



$\widehat{S\,S}$ = S_2CNMe_2

Figure 3.

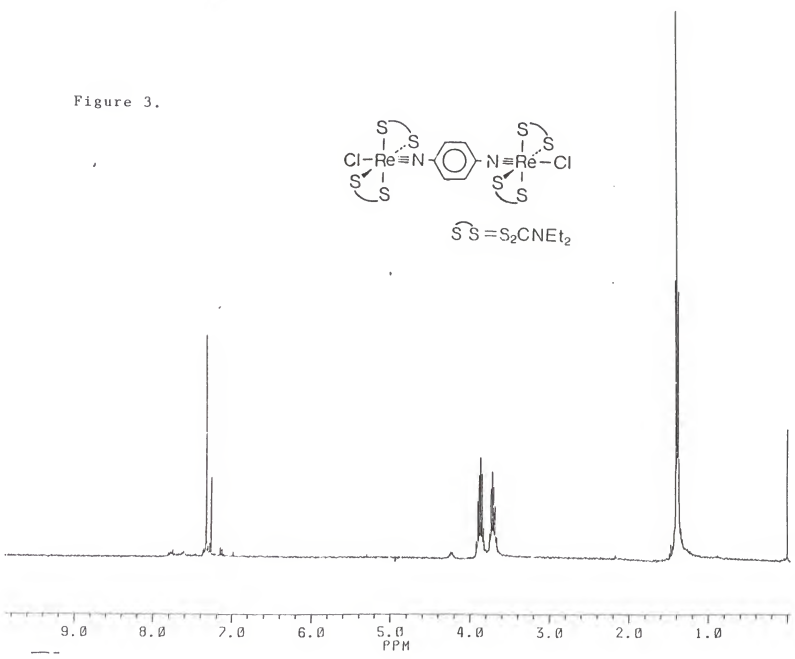


Figure 4.

$\widehat{SS} = S_2CN(i\text{-}Pr)_2$

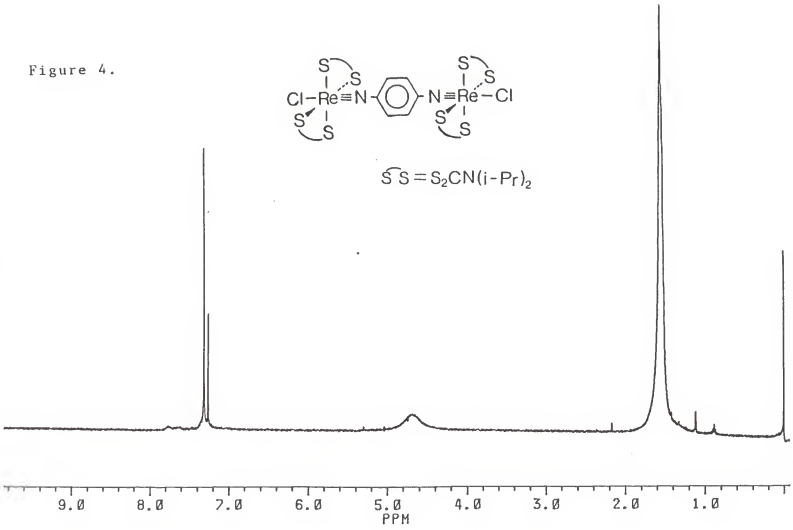


Figure 5.

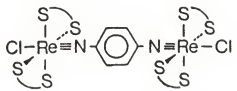


Figure 6.

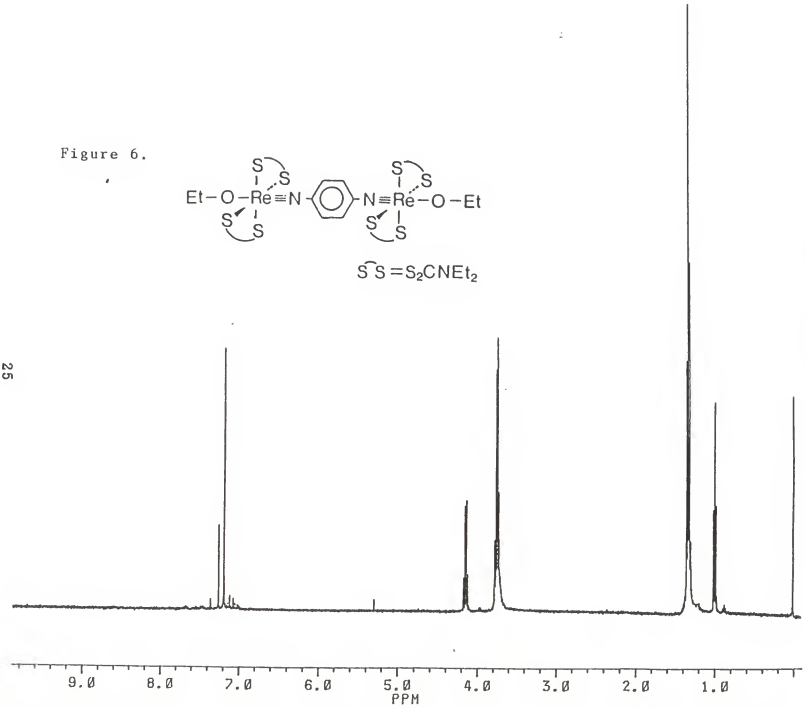
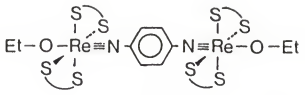


Figure 7.



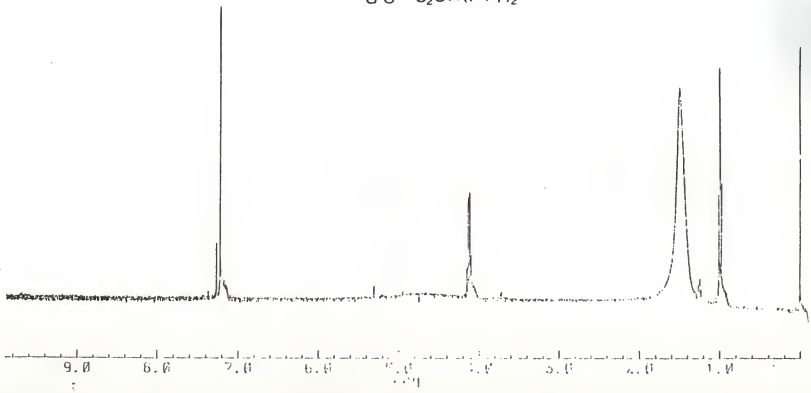


Figure 8.

$\overset{\frown}{S\,S} = S_2CNEt_2$

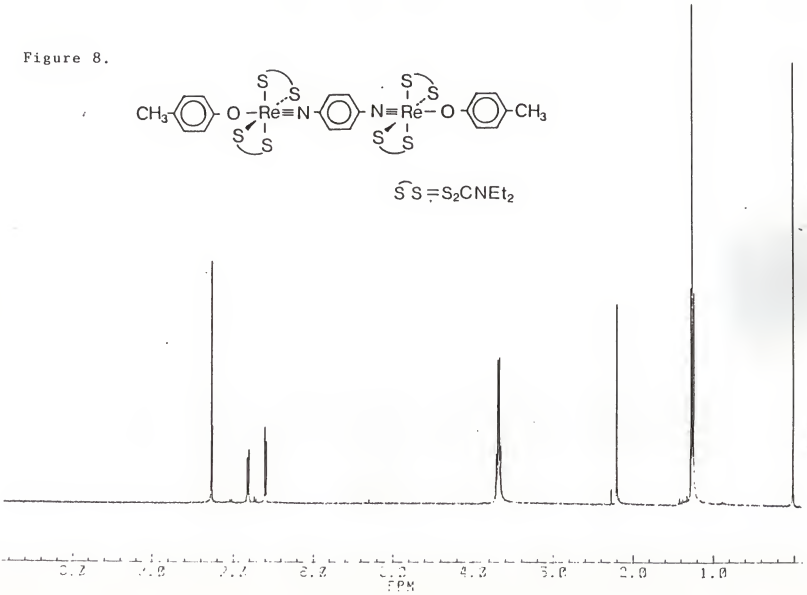


Figure 9.

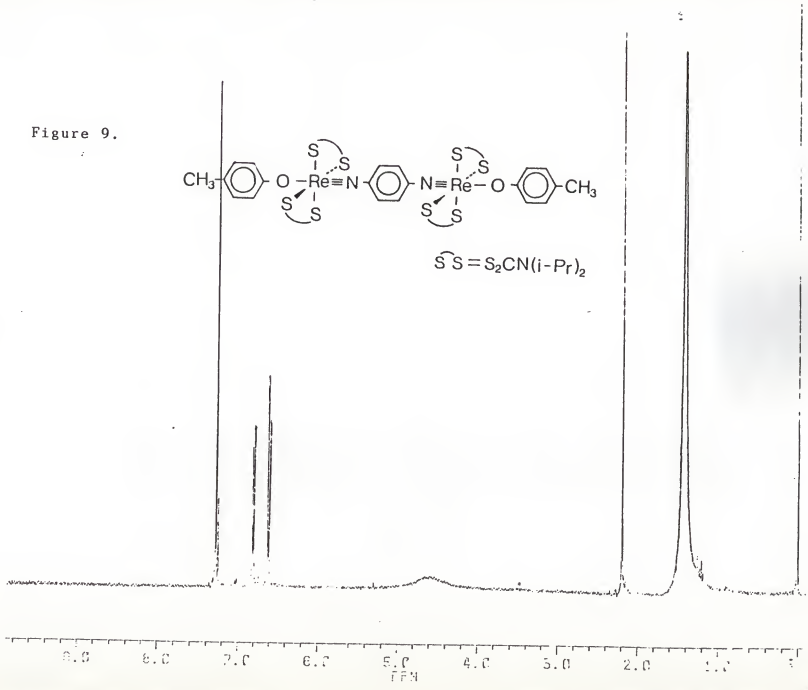
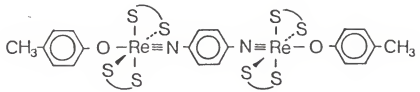


Figure 10. ^{1}NMR Spectrum of 4b at -30°C.



$\overset{\frown}{S\,S} = S_2CN(i\text{-}Pr)_2$

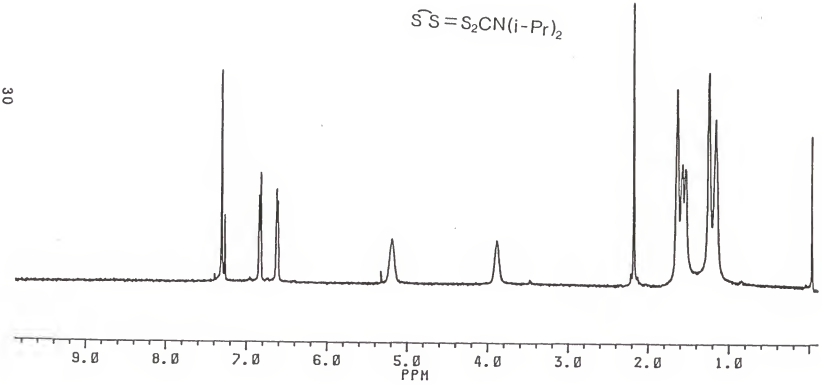
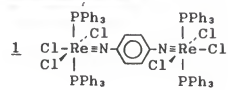
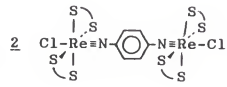


Table 1. ^{1}H NMR DATA.

Compounds		$N-C_6H_4-N$	$-NR_2$		Others	
1		6.52(s)	-		PPh_3	7.22(broad) 7.70(broad)
2						
2d	S⌒S = Me_2dtc	7.35(s)	-N-C<u>H</u>$_3$	3.38(s)	-	
2a	Et_2dtc	7.33(s)	-N-C<u>H</u>$_2$CH$_3$	3.86(m), 3.71(m)	-	
			-N-CH$_2$C<u>H</u>$_3$	1.38(t; J=7.2Hz)		
2b	$(i\text{-}Pr)_2dtc$	7.31(s)	-N-C<u>H</u>$(CH_3)_2$	4.7(broad)	-	
			-N-CH$(CH_3)_2$	1.53(broad)		
2c	$(C_6H_{11})_2dtc$	7.29(s)	*		-	

* Complicated Peaks

(Continued)

Table 1. ^{1}H NMR DATA (Continued)

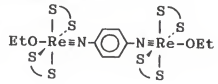
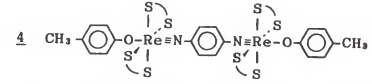
Compounds	N-C$_6$H$_4$-N	-NR$_2$	others
3 			
3a S⌒S = Et$_2$dtc 7.19(s)		-N-C$\underline{H}_2$CH$_3$ 3.75(q;J=7.2)	-O-C$\underline{H}_2$CH$_3$ 4.14(q;J=7.0)
		-N-CH2C$\underline{H}_3$ 1.33(t;J=7.2)	-O-CH$_2$C$\underline{H}_3$ 1.00(t;J=6.9)
3b (i-Pr)$_2$dtc 7.21(s)		-N-C$\underline{H}$(CH$_3$)$_2$ 4.7(broad)	-O-C$\underline{H}_2$CH$_3$ 4.12(q; J=6.9)
		-N-CH(C$\underline{H}_3$)$_2$ 1.50(broad)	-O-CH$_2$C$\underline{H}_3$ 1.00(t; J=6.9)
4 			
4a S⌒S = Et$_2$dtc 7.27(s)		-N-C$\underline{H}_2$CH$_3$ 3.68(q;J=7.3)	-O-C$_6\underline{H}_4$-CH$_3$ 6.81(d;J=8.1)
		-N-CH$_2$C$\underline{H}_3$ 1.25(t;J=7.2)	6.59(d;J=8.4)
			-O-C$_6$H$_4$-C$\underline{H}_3$ 2.20(s)
4b (i-Pr)$_2$dtc 7.28(s)		-N-C$\underline{H}$(CH$_3$)$_2$ 4.6(broad)	-O-C$_6\underline{H}_4$-CH$_3$ 6.61(d;J=8.3)
		-N-CH(C$\underline{H}_3$)$_2$ 1.43(broad)	6.61(d;J=8.4)
			-O-C$_6$H$_4$-C$\underline{H}_3$ 2.19(s)

Table 1. (continued)

All spectra were taken in $CDCl_3$ at ambient temperature.
Chemical shifts are parts per million(ppm) downfield of internal TMS standard; s: singlet, d: doublet, t: triplet, q: quartet, m:multiplet, broad: broad peak, J: coupling constant in Hz.

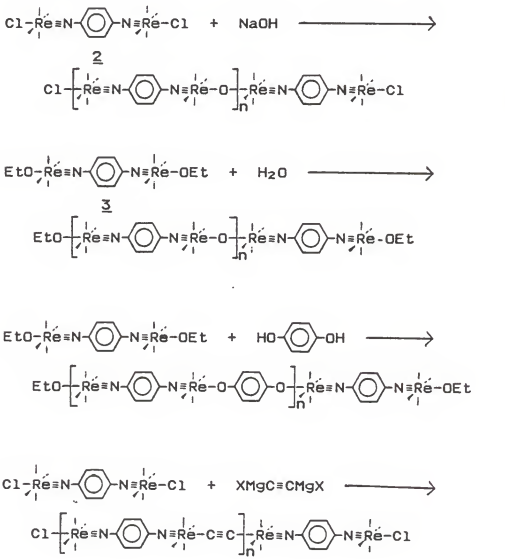
Table 2. Elemental Analysis Results.

Complexes		Calculated %C	Calculated %H	Calculated %N	Found %C	Found %H	Found %N
1	$C_{78}H_{64}Cl_6N_2P_4Re_2$	53.89	3.71	1.61	53.83	3.73	1.80
2a	$C_{26}H_{44}Cl_2N_6Re_2S_8$	27.38	3.89	7.37	27.72	3.80	6.91
4b	$C_{48}H_{74}N_6O_2Re_2S_8$	41.30	5.34	6.02	41.34	5.33	5.39

III. THE POLYMERIZATION OF p-PHENYLENEDIIMIDO COMPLEXES

The polymerization of p-phenylenediimido complexes of rhenium can be achieved by replacing terminal ligands with difunctional ligands as bridging units. Some possible routes are represented in scheme II.

SCHEME II.



(A)

(B)

(C)

(D)

There seems to be little doubt that reactions (A), (B), and (C) would go because the reactions with similar monomeric compounds, such as NaOEt or $HO-C_6H_4-CH_3$, are spontaneous and clear as mentioned in section II. Furthermore, oxo bridged species, $(Tol-N)(Me_2NCS_2)_2Re-O-Re(S_2CNMe_2)_2(N-Tol)$, was made from the reaction of $(Tol-N)(Me_2NCS_2)_2Re(OEt)$ and H_2O[17].

Reaction of ethoxy complex(3) and H_2O

To a suspension of Re complex in CH_2Cl_2 solution was added several drops of water:

$\widehat{S\,S} = S_2CNEt_2$

The color was changed from yellow to dark purple immediately. The black precipitate, 5, was filtered and washed with acetone. IR; 1272(s), 1214(s), 1154(s), 1097(w), 1081(m), 917(m), 849(s), 787(w), 694(s), 666(m), 561(m), 518(w).

This product is thought to be a polymer bridged by Re-O-Re bonds and has 694cm^{-1} peak in IR spectrum. This peak is tentatively assigned to the Re-O-Re asymmetric stretching mode, which ranges from 670 to 730cm^{-1} in similar

Table 3 IR Spectra for Re-O-Re Asymmetric stretching Mode

Compounds	Re-O-Re/cm^{-1}	References
$[ORe(S_2CNEt_2)_2]_2O$	$670cm^{-1}$	11
$[Re(NPh)(S_2CNEt_2)_2]_2O$	660	11
$[ORe(CN)_4]_2O^{4-}$	720	18
$[OReCl_2en]_2O$	730	19
	720	18
$[OReCl_2py_2]_2O$	675	19
	710-675	11,18

complexes(Table 3). This $694cm^{-1}$ peak shifted to $679cm^{-1}$ and $660cm^{-1}$ when ^{17}O and ^{18}O labeled H_2O was used(^{17}O:46.5%, ^{18}O:41.2%)(Figure 11). The theoretical values for three atomic Re-^{17}O-Re and Re-^{18}O-Re antisymmetric stretching modes are $674cm^{-1}$ and $656cm^{-1}$ respectively if we assign the $694cm^{-1}$ peak to Re-^{16}O-Re antisymmetric stretching mode. This is a good evidence for the presence of Re-O-Re bonds and, as a result, the oxo bridged polymer.

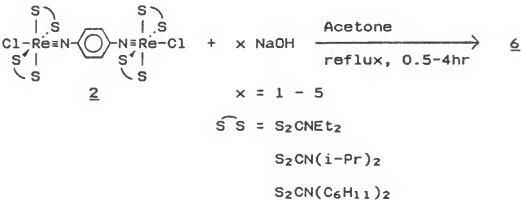
Figure 12 shows the change of ^1H NMR spectrum upon addition of water. The bottom spectrum is the original NMR spectrum of species 3. After a drop of water was added, the original peaks disappeared gradually due to the formation of insoluble polymers and free ethanol peaks grew

up at 1.25ppm(t;3H), 3.71ppm(q;2H), and 4.52ppm(broad;1H).

However, the investigation of the degree of polymerization was not possible because complex 5 was insoluble in any organic solvents. We tried to make this species soluble by using more bulky di(iso-propyl) and di(cyclohexyl)dithiocarbamate complexes but similar results were observed.

Reaction of Chloro complex(2) and NaOH.

Complex 2 was added to acetone solution containing x equivalents of NaOH; freshly cut Na metal was dissolved in 1mL of H_2O:

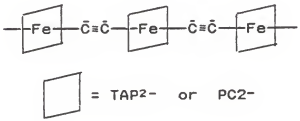


The mixture was refluxed for 0.5-4 hours and the color changed to dark purple. The black precipitate was filtered and washed with water and acetone. Insoluble product 6 was obtained regardless of reaction time nor the ratio of NaOH.

IR spectra of these products also show Re-O-Re stretching modes around 696cm^{-1}.

Reaction of Species 2 and acetylides.

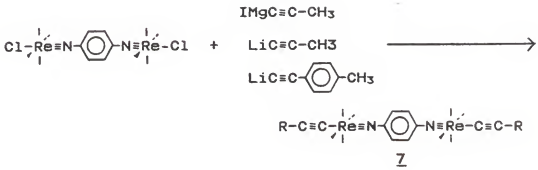
The product of reaction (D) of scheme II, which is bridged by acetylenic group (-C≡C-), could be the best system for the purpose of pi-electron conjugation and, as a result, for electrical conduction. Semiempirical extended Hückel molecular orbital(EHMO) calculation has been done for a model system by Hanack and co-workers[20]:



In this system, tetraazaporphin or phthalocyanine macrocycles centered by Fe ion are linked by acetyleinic bridges. According to their calculation the energy band was partially filled reaching approximate Fermi level and metal-like electrical conduction was expected through the one-dimensional chain.

For the preliminary investigation for the reaction (D), we tried the reaction of species 2 and methyl or p-tolyl

acetylenic complexes:



7

But every effort to make complex 7 was unsuccessful. The reaction products seemed quite unstable and sometimes dissociation of dithiocarbamate ligands was observed.

Figure 11. Partial IR Spectra of p-Phenylendiimido Complexes.

a. $(EtO)(Et_2NCS_2)_2Re{\equiv}N$-  -$N{\equiv}Re(S_2CNEt_2)_2(OEt)$ (3a).

b. The reaction product of 3a and H_2O; 694cm^{-1} peak is assigned to the Re-O-Re asymmetric stretching mode.

c. The reaction product of 3a and labeled H_2O (^{17}O:46.5%, ^{18}O:41.2%); 694cm^{-1} peak shifts to 679cm^{-1} and 660cm^{-1}.

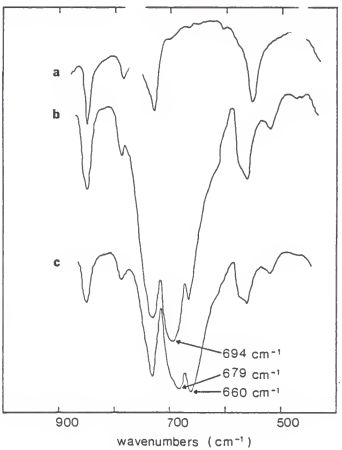
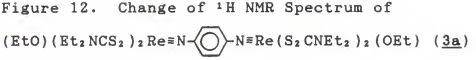


Figure 12. Change of ^1H NMR Spectrum of

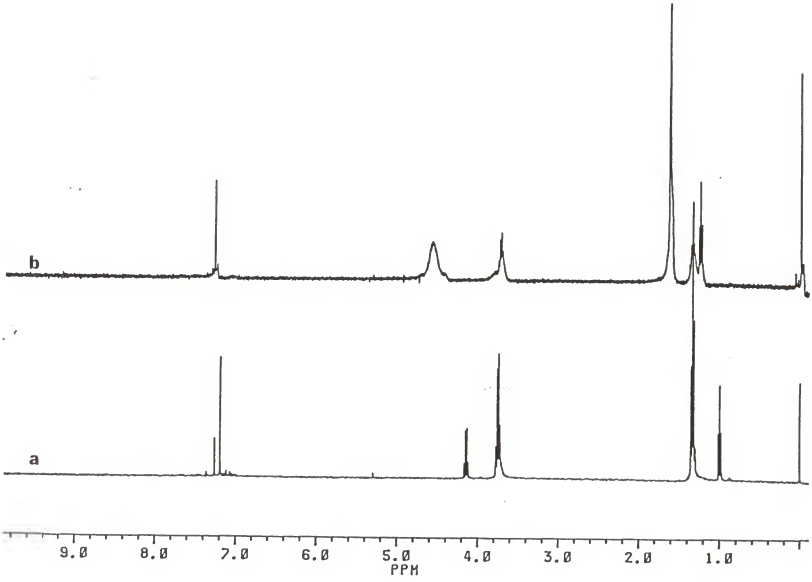


(3a)

upon addition of H_2O.

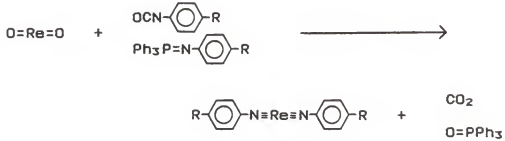
a. Original Spectrum.

b. Spectrum showing the CH_3CH_2OH peaks liberated by the reaction.


b
a
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
PPM

APPENDIX: trans-Diimido Complexes of Rhenium.

We tried to make trans-diimido complexes of rhenium from their isoelectronic trans-dioxo complexes:



We also expected to make polymeric compounds by using trans-dioxo rhenium compexes and diisocyanate or bis(triphenyl phosphine).

A lot of trans-dioxorhenium complexes have been reported and we used $[ReO_2(py)_4]^+$ [21], $[ReO_2(en)_2]^+$ [22], $[ReO_2(CN)_4]^{3-}$, and $Re_2O_3(S_2CNEt_2)_4$ [11]. But these reactions didn't go cleanly.

REFERENCES

1. (a) T. A. Skotheim (Ed.), "Handbook of Conducting Polymers", Vol. 1 & 2, Marcel Dekker, 1986.
   (b) L. Alcacer (Ed.), "Conducting Polymers", D. Reidel, Holland, 1987.
2. G. Natta, G. Mazzaniti, and P. Corradini, Atti. Accad. Naz. Limce, Red. Cl. Sci. Fis, Mat. Nat., 8, 3(1958).
3. (a) H. Shirakawa, E. J. Louis, A. G. MacDiarmid. C. K. Chiang, and A. J. Heeger, J. Chem. Soc., Chem. Comn., 578(1977).
   (b) C. K. Chiang, M. A. Druy, S. C. Gau, A. J. Heeger, E. J. Louis, A. G. MacDiarmid, Y. W. Park, and H. Shirakawa, J. Am. Chem. Soc., 100, 1013(1978).
4. (a) O. Schneider, M. Hanack, Angew. Chem. Int. Ed. Engl. 19, 392(1980).
   (b) F. Kubell and J. Strahle, Z. Naturforsch., 37b, 272 (1982).
   (c) V. J. Metz and M. Hanack, J. Am. Chem. Soc., 105, 828(1983).
   (d) B. N. Diel, T. Inabe, N. K. Jaggi, J. W. Lyding, O. Schneider, M. Hanack, C. R. Kannewurf, T. J. Marks, and L. H. Schwartz, J. Am. Chem. Soc., 106, 3207 (1984).
   (e) M. Hanack and W. Kobel, Inorg. Chem., 25, 503(1986).

(f) J. P. Collman, J. T. McDevitt, C. R. Leidner, G. T.Yee, J. B. Torrance, and W. A. Little, J. Am. Chem. Soc., 109, 4606(1987).

5. E. A. Maatta and D. D. Devore, Angew. Chem. Int. Ed. Engl., in press (1988).

6. (a) A. J. Lee, J. M. Fobare, and E. F. Mattimore, Inorg. Chem., 23, 2703(1984).

(b) R. Gross and W. Kaim, Inorg, Chem., 25, 498(1986).

7. N. A. Milas and I. M. Iliopulos, J. Am. Chem. Soc., 81, 6089(1959).

8. W. A. Nugent and B. L. Haymore, Coord. Chem. Rev., 31, 123(1980).

9. E. A. Maatta, B. L. Haymore and R. A. D. Wentworth, J. Am. Chem. Soc., 101, 2063(1979).

10. A. O. Chong, K. Oshima, and K. B. Sharpless, J. Am. Chem. Soc., 99, 3420(1977).

11. J. F. Rowbottom and G. Wilkinson, J. Chem. Soc., Dalton Trans., 826(1972).

12. K. L. Wall, J. C. Huffmann, and R. A. D. Wentworth, Inorg. Chim. Acta, 86, L25(1984).

13. D. D. Devore, Ph. D. Dissertation, Kansas State University (1987).

14. J. Chatt and G. A. Rowe, J. Chem. Soc., 4019(1962).

15. D. L. Herring, J. Org. Chem., 26, 3998(1961).

16. J. Chatt, J. D. Johnson, and G. A. Rowe, J. Chem. Soc., 1012(1964).

17. G. V. Goeden and B. L. Haymore, Inorg. Chem., 22, 157 (1983).

18. H. E. Howard-Lock, C. J. L. Lock, and G. Turner, Spectrochimica Acta, 38A, 1283(1982).

19. Jezowska-Trzebiatowska, J. Hunuza, and M. Baluka, Spectrochima Acta, 27A, 1753(1971).

20. (a) M. Hanack, F. F. Seelig, and J. Strahle, Z. Naturforsch, 34a, 983(1979).
(b) F. F. Seelig, ibid., 34a, 986(1979).

21. N. P. Johnson, C. J. L. Lock, and G. Wilkinson, J. Chem. Soc., 1054(1964).

22. C. J. L. Lock and G. Wilkinson, J. Chem. Soc., 228(1964).

ACKNOWLEDGEMENT

I would like to express my appreciation to my major professor, Dr. Eric Maatta, for his encouragement and support of this research and my graduate studies. I would also like to thank to my graduate committee members, Dr. David Macomber and Dr. Duy Hua.

To my wife, Sunah, I express special appreciation for her patience and understanding.

THE SYNTHESIS OF p-PHENYLENEDIIMIDO COMPLEXES OF RHENIUM(V)

by

CHANGMIN KIM

B.S., Seoul National University, Korea, 1983

AN ABSTRACT OF A THESIS

submitted in partial fulfillment of the
requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1988

A p-phenylenediimido complex of rhenium(V), $Cl_3(PPh_3)_2Re{\equiv}N\text{-}C_6H_4\text{-}N{\equiv}Re(PPh_3)_2Cl_3$ [1], has been prepared from $ReOCl_3(PPh_3)_2$ and $Ph_3P{=}N\text{-}C_6H_4\text{-}N{=}PPh_3$. Complex 1 reacts with thiuram disulfides to produce $Cl(R_2NCS_2)_2Re{\equiv}N\text{-}C_6H_4\text{-}N{\equiv}Re(S_2CNR_2)_2Cl$ [2] (R= CH_3, C_2H_5, $CH(CH_3)_2$, or cyclohexyl). Complex 2 reacts with sodium ethoxide to give $(EtO)(R_2NCS_2)_2Re{\equiv}N\text{-}C_6H_4\text{-}N{\equiv}Re(S_2CNR_2)_2(OEt)$ [3]. The reaction of 3 and p-cresol produces $(Tol\text{-}O)(R_2NCS_2)_2Re{\equiv}N\text{-}C_6H_4\text{-}N{\equiv}Re(S_2CNR_2)_2(O\text{-}Tol)$ [4].

Polymerization of species 2 and 3 has been investigated. Although the insolubility of polymerization products prevented detailed analysis, IR and NMR results support the presence of polymeric species.